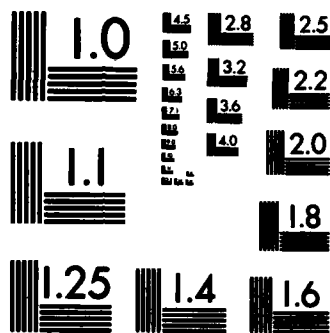END

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Mixed-valence, intervalence transfer, metallopolymer, modified electrode.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report covers work done by the author in both mixed-valence dimers and metallopolymers. Concerning the dimers, crystal structures of related monomers were obtained to judge the adequacy of classical approximations in calculating inner-sphere vibrational trapping. A series of homometallic and heterometallic dimers were prepared and a relationship between redox asymmetry and intervalence transfer absorption band energy was found. Electronic structure was observed in the intervalence transfer absorption band of an

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20. Os(II)-Os(III) mixed-valence dimer, owing to the presence of well-separated spin orbit states in Os(III). Other dimers were prepared to study the transitions between various states within the dimers. Both metal to metal and ligand to ligand electron transfer was seen in optically prepared mixed-valence dimers. Concerning the polymers, redox-site incorporation into poly-vinylpyridine, p-chlorosulfonated polystyrene and oxidatively electro-polymerized films were studied. Characterization and stability of these films as well as comparison to monomeric analogues was accomplished. Practical application of the metallopolymers include their use as a chromophore in a photoelectrochemical cell and as a catalyst for the oxidation of Cl^- to Cl_2.

CHARGE TRANSFER IN MULTIPLE SITE CHEMICAL SYSTEMS

FINAL REPORT

Thomas J. Meyer
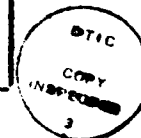
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With support from the Army Research Office we have been engaged in research involving charge transfer processes in chemical systems that contain more than one redox site. The systems include both ligand-bridged metal dimers and polymeric materials where the redox sites are incorporated either by ion exchange or by direct chemical linkage into a polymeric backbone.

Our work with mixed-valence dimers has taken two directions. First, we have been interested in the various contributions to the energy of the intervalence transfer (IT) band in weakly coupled mixed-valence dimers. It has been recognized for some time that these contributions come from reorganization of inner sphere and outer sphere (solvent) vibrational modes as well as the internal energy difference ($\triangle E$) between the two sites[1]. To probe the inner sphere contributions to electron transfer, x-ray crystal structures of the complexes cis-$Ru^{II}(bpy)_2Cl_2 \cdot 3.5 H_2O$ and cis-$[Ru^{III}(bpy)_2Cl_2]Cl \cdot 2H_2O$ (bpy is 2,2'-bipyridine) were obtained.[2] The most important result is the significant shortening (0.10 Å) of the Ru-Cl bond upon oxidation from Ru^{II} to Ru^{III}, a slighter increase (0.04 Å) in the Ru-N distances trans to the Ru-Cl bonds, and the virtual insensitivity (a 0.006 Å increase) in the Ru-N distances cis to the Ru-Cl bonds. This suggests that electrostatic effects are primarily responsible for changes in Ru-Cl bond lengths, but that the poorer π-backbonding from Ru^{III} to the pyridyl ligands compensates for stronger electrostatic attraction between metal and ligand. An analysis of the contribution of intramolecular vibrations to the vibrational barrier to electron transfer for the $Ru(bpy)_2Cl_2^{+/o}$ couple based on the structures and available vibrational information shows that the Ru-Cl bonds make the primary contribution to the inner sphere reorganizational energies (λ_i). The analysis also showed that the classical approximation is

adequate to calculate λ_i when vibrational trapping has its origins in low frequency metal-ligand modes.

To probe the relationship between redox asymmetry and IT absorption band energy, a series of symmetrical Ru-Ru and mixed-metal Ru-Os dimers were prepared and their spectral properties were compared with electrochemical data.[3] The mixed-valence dimers, $[(bpy)_2ClRu(B)MCl(bpy)_2]^{3+}$, $[(bpy)_2Ru(bpm)M(bpy)_2]^{5+}$, and $[(bpy)_2ClRu(pyzc)M(bpy)_2]^{3+}$ (B = pyrazine, 4,4-bipyridine; bpm = 2,2'-bipyrimidine, pyzc = 2-pyrazine carboxylate anion; M = Ru, Os), all display broad low energy, intervalence transfer absorption bands which have the properties expected for optically induced electron transfer between weakly coupled metal centers. For the mixed metal dimers, the IT bands are observed at a systematically higher energy than IT bands in analogous Ru^{II}-Ru^{III} analogs consistent with the redox asymmetry in the dimers and the equation, $E_{op} = \chi + \Delta E$ where E_{op} is the energy of the optical transition, χ is the vibrational trapping or reorganizational energy and ΔE the internal energy change. IT bandwidths at half-height ($\Delta\bar{\upsilon}_{\frac{1}{2}}$) for analogous pairs of Ru-Ru and Ru-Os dimers and similar and predicted by the Hush equation ($\Delta\bar{\upsilon}_{\frac{1}{2}} = [16(\ln2) \times k_B T]^{\frac{1}{2}}$) suggesting that vibrational reorganizational energies are comparable for the two types of dimers. The increase in E_{op} for the unsymmetrical dimers can be accounted for quantitatively in terms of the internal energy change ΔE. Given the similarities in molecular volumes between the Ru and Os sites, a thermodynamic analysis shows that ΔE can be calculated from reduction potential data for the Ru(III)/(II) and Os(III)/(II) couples in the dimers. As calculated from IT band intensities, the extent of delocalization between M(II) and M(III) sites in the mixed-valence dimers, α^2, is comparable for the Ru^{II} - Ru^{III} and

Ru^{II}-Os^{III} dimers, suggesting that electronic coupling between metal centers is dominated by Ru^{II} mixing with the bridging ligand.

In addition to energy considerations in characterizing an IT band, the possibility of electronic structure in the band exists in dimers which involve Ru^{III} and Os^{III} as a product after the electron transfer. Electronic structure has been observed in the intervalence transfer absorption band of the weakly coupled mixed-valence dimer, $[(bpy)_2ClOs^{II}(PPh_2CH_2Ph_2P)Os^{III}Cl(bpy)_2]^{3+}$.[4] The origin of the structure lies in the large spin-orbit (SO) coupling constant (λ_{Os}) for osmium which leads to well separated SO states for the Os^{III} $d\pi^5$ electronic configuration. For Os^{III}-bpy monomers, low energy $d\pi \rightarrow d\pi$ transition bewteen the SO states are observed in the near-infrared (NIR). Optical electron transfer in the mixed-valence dimer results in the formation of a "new" Os(III) site in one of three possible SO state ($1E'$, $2E'$ or $3E'$), and hence the IT manifold should contain three components separated by the energy differences between the SO states at the Os(III) site. In addition to the expected $d\pi$-$d\pi$ absorption bands, the spectrum of the Os(II)-Os(III) dimer in the NIR shows two broad, solvent-dependent bands which are assignable to IT transitions. The bands are separated in energy by approximately the energy difference between the two lowest SO states as expected. Calculations on the expected position of the third component indicate that it should occur in a spectral region obscured by intense metal-to-ligand charge transfer bands. By analogy, it is argued that the single IT band observed for the Ru dimer, $[(bpy)_2ClRu^{II}(PPh_2CH_2Ph_2P)Ru^{III}Cl(bpy)_2]^{3+}$, also consists of a manifold of three closely spaced components, but that they are not resolvable at room temperature because of the smaller SO coupling constant for $Ru(\lambda_{Ru} \sim 1/3\lambda_{Os})$. For the Ru dimer, the IT band intensity is expected to be dominated by the transition $Ru^{II}(A_1)$-$Ru^{III}(1E') \rightarrow Ru^{III}(2E')$-$Ru^{II}(A_1)$, which

occurs at <u>ca</u>. 1700 cm^{-1} above the lowest energy transition, $Ru^{II}(A_1)-Ru^{III}(1E')$ $\rightarrow Ru^{III}(1E')-Ru^{II}(A_1)$. As a consequence, the use of the IT band energy to estimate the classical inner-sphere vibrational trapping energy, $\times_i/4$, from solvent dependence studies is an overestimate for this and related dimers.

In the second direction we have taken in our ARO sponsored work with mixed-valence dimers, we have been concerned less with the shape and position of the IT band, but more interested in the actual movement of the electrons within the dimers. In the first of these sytems, we attempted to probe the quenching of a state where the excess electron resides not on either metal, but on the bridging ligand.[5] We found that one-electron oxidation of the dimers $(dpte)_2ClRu^{II}(L)Ru^{II}Cl(bpy)_2^{2+}$ (dpte is $PhSCH_2CH_2SPh$; L is 4,4'-bipyridine(4,4'-bpy); <u>trans</u>-bis-4-pyridylethylene (bpe); or 1,2-bis-4-pyridylethane(bpa)) gives the corresponding mixed-valence dimers $(dpte)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2^{3+}$. In the mixed-valence dimers, Ru(II) $\rightarrow$ Ru(III) intervalence transfer bands are observed. Photolysis into either the $\pi^*(bpy)\leftarrow d\pi(Ru^{II}Cl(bpy)_2)$ chromophore for the Ru(II)-Ru(II) dimers or the $\pi^*(L)\leftarrow d\pi(Ru^{II}Cl(dpte)_2)$ chromophore for the mixed-valence dimers results in population of the bpy-based, ^{3}MLCT excited state (-$Ru^{III}Cl(\overline{bpy})(bpy)^*$) as shown by comparisons between room temperature emission and low temperature (220-280K) transient absorption properties of the dimers and the related monomers, $(bpy)_2ClRu(L)^+$. The appearance of the ^{3}MLCT-bpy based emission in the mixed-valence dimers shows that the following $\pi^*(L)\leftarrow d\pi(Ru^{II}Cl(dpte)_2)$ excitation, ligand to ligand electron transfer, $(dpte)_2ClRu^{III}(\overline{L})Ru^{III}Cl(bpy)_2^{3+*} \rightarrow (dpte)_2ClRu^{III}(L)Ru^{III}Cl(\overline{bpy})(bpy)^{3+*}$, occurs and is competitive with excited state nonradiative decay by ligand to metal electron transfer, $(dpte)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2^{3+} \leftarrow (dpte)_2ClRu^{III}(\overline{L})Ru^{III}Cl(bpy)_2^{3+*}$

$\longrightarrow (dpte)_2ClRu^{III}(L)Ru^{II}Cl(bpy)_2^{3+}$. Because of the relatively long lifetime of the ^3MLCT-bpy state, it is not possible to observe relaxation of the high energy, mixed-valence isomer to the ground state, $(dpte)_2ClRu^{III}(L)Ru^{II}Cl-(bpy)_2^{3+} \rightarrow (dpte)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2^{3+}$, following nonradiative decay of ^3MLCT-bpy. For the pentaammine Ru(II) dimers, $(NH_3)_5Ru^{II}(L)Ru^{II}Cl(bpy)_2^{3+}$, (L = bpe, 4,4'-bpy) excitation into the $\pi^*(bpy) \leftarrow d\pi(Ru^{II})$ chromophore does not lead to emission or transient decay from the ^3MLCT-bpy excited state apparently because of intramolecular energy transfer to lower lying, relatively short-lived $(NH_3)_5Ru^{III}(\overset{\text{-}}{L})$-based MLCT states. The ^3MLCT-bpy excited state is also not observed following $\pi^*(bpy) \leftarrow d\pi(Ru^{II})$ excitation in the mixed-valence dimers, $(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bpy)_2^{4+}$ (L = 4,4'-bpy,bpe) either because of intramolecular quenching by Ru(III) or perhaps because of population of short-lived MLCT states based on the bridging ligand, $(NH_3)_5Ru^{III}(\overset{\text{-}}{L})$-.

In the second of these systems, we studied an "optically prepared" mixed-valence dimer, which was formed as the result of a metal-to-ligand-charge-transfer (MLCT) on one side of an asymmetric Os^{II}-Os^{II} dimer.[6] To understand the electronic processes in this type of system, we studied the photophysics of the unsymmetrical, ligand-bridged Os dimers,
$[(bpy)_2(CO)Os^{II}(L)Os^{II}(phen)(dppe)(Cl)]^{3+}$ and
$[(bpy)_2(CO)Os^{II}(L)Os^{III}(phen)(dppe)(Cl)]^{4+}$ (where L = 4,4'-bipyridine (4,4'-bpy) or bis-1,2(4-pyridyl)ethane (bpa), phen = 1,10-phenanthroline and dppe = bis-1,2(diphenylphosphino)-cis-ethene). In the (II,II) dimers, two independent MLCT chromophores are present, based upon the localized $d\pi(Os) \rightarrow phen$ and $d\pi(Os) \rightarrow$ 2,2'-bpy transitions at the respective metal centers. The results of transient absorption and emission experiments indicate that quenching of the higher energy, Os-bpy MLCT state, occurs via reductive electron transfer from the adjacent Os-

phen site and not by energetically favorable Os-bpy MLCT → Os-phen MLCT energy transfer. Rate constants for intramolecular electron transfer have been measured for the bpa-bridged dimer at low temperatures in a solvent glass. The excited state behavior of the two (II,II) dimers (L = 4,4'-bpy or bpa) is found to be similar in frozen solvents, however, the photophysical characteristics of the 4,4'-bpy bridged dimer change dramatically at the glass to fluid transition of the solvent. Steady state and dynamic emission experiments along with transient absorbance data indicate that the change in excited state behavior for the 4,4'-bpy dimer has its origin in the ability of the 4,4'-bpy bridging ligand to "flatten" and act as an electron acceptor. The flattening and concomittant intramolecular quenching process only occur in a fluid medium where they are rapid compared to the intrinsic lifetime of the initially populated CT excited state. In the mixed-valence (II,III) dimers the spectroscopically observed excited state is based on the $d\pi(Os) \rightarrow 2,2'$-bpy MLCT transition. Suprisingly, in the mixed-valence dimers the adjacent Os^{III}-phen site does not quench the relatively long-lived Os-bpy excited state by any of a number of energetically favorable pathways.

In addition to quenching of an excited state by a metal ion in an optically prepared mixed-valence dimer, we have also demonstrated intramolecular excited state quenching by ligand which can act as an electron donor.[7]

The chromophore-quencher complex $[(bpy)Re^{I}(CO)_3(py-PTZ)]^{+}$ has been prepared and its photophysical properties investigated by transient absorption and emission measurements.
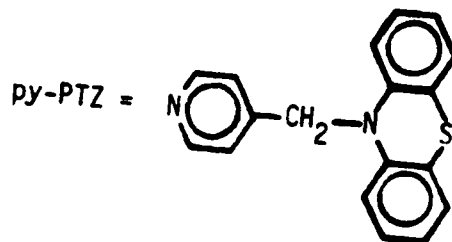
py-PTZ =

Initial optical excitation gives the bpy-based metal-to-ligand charge transfer state $[(\overline{bpy})Re^{II}(CO)_3(py-PTZ)]^+$ which is rapidly quenched (τ<10ns) in fluid solution at room temperature by intramolecular ligand-to-metal charge transfer to give the charge-separated state $[(\overline{bpy})Re^I(CO)_3(py-PTZ^+)]^+$. The lifetime of the charge-separated state is 25ns at room temperature in acetonitrile by transient absorption decay measurements.

Much of our work in polymers containing multiple redox sites has been concerned with the preparation and characterization of the polymers. A major theme has been the comparison of metallopolymeric properties to those of monomeric analogues. The polymeric materials are of interest for their potential applications in such areas as catalysis, photoredox systems, and studies of the fundamental properties of film-coated electrodes.[8]

One method of attachment of metal complexes to a polymer is the reaction of Ru complexes with poly(4-vinylpyridine) (PVP) where in the final polymer, the vinylpyridine groups act as ligands toward the metal.[9]

We have prepared a series of metallopolymers and investigated their chemical and physical properties. The work has led to a number of important conclusions which are summarized below:

1) Preparation of the metallopolymers can be accomplished using synthetic procedures which are based on the known chemistry of monomeric analogues.

2) The polymer-bound metal complex sites retain the chemical and physical properties inherent in related monomers, as shown by spectral measurements and the observation of net reactions of the various materials in homogeneous

solutions.

3) Interestingly, modifications in the chemical and redox reactivities of the polymer-bound sites do occur in certain cases when the metallopolymers are examined as films evaporatively deposited onto electrode surfaces. The origin of the differences is believed to be due to two major factors:

A) <u>Spatial</u> <u>separation</u> of the chemical sites along the polymer chain can change the net chemistry by slowing or eliminating bimolecular reactions with strict orientational demands, e.g.:

$$Ru^{III}(bpy)_2(PVP)(ONO)^{2+} + Ru^{III}(bpy)_2(PVP)(NO_2)^{2+} \rightarrow Ru^{II}(bpy)_2(PVP)(ONO_2)^+ + Ru^{II}(bpy)_2(PVP)(N^+O)^{3+}$$
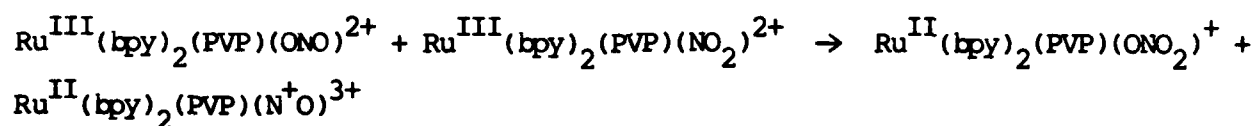
B) Changes in the <u>local</u> <u>environment</u> at the chemical sites due to the presence of protonated or unprotonated pyridyl groups from the main chain of the polymer can also change the net chemistry, e.g.,

i) The loss of pH dependence for the Ru(III/II) couple of $Ru(bpy)_2(PVP)(OH_2)^{2+}$ at pH>4.

ii) The change in the course of the decomposition chemistry of $Ru(bpy)_2(PVP)(N_3)^{2+}$ where a labile intermediate appears to be captured by an unbound pyridyl group rather than by solvent.

iii) The decrease in rates of chemical reactions within the film environment, e.g., the slowness of the aquation of Ru^{II}-chloro and Ru^{II}-ONO_2 sites, of nitro-nitrosyl interconversion and of H/D exchange at Ru^{II}-aquo sites.

Another method of attachment is based on the reaction of the redox couple with p-chlorosulfonated polystyrene.[10] Redox couples which contain unbound amine, hydroxy or carboxylate groups can be incorporated at room temperature into

p-chlorosulfonated polystyrene films via sulfonamide, sulfonester, or sulfonanhydride linkages, respectively. The p-chlorosulfonatea polystyrene films can be cast onto virtually any surface, including platinum and glassy carbon electrodes. The redox couples incorporated include polypyrydyl complexes of iron, ruthenium and osmium, an ammine complex of ruthenium, organics, a nickel macrocycle and a nickel porphyrin. The modified films based on sulfonamide links were the most stable and the films based on sulfonanhydride links were by far the least stable. The p-chlorosulfonated polystyrene films were used in a variety of applications including: 1) Coincorporation of more than one redox site; 2) Fabrication of bilayer structures in which different redox couples are held in spatially segregated films; 3) Selectivity and directed charge transfer effects involving redox couples in the external solution; 4) Hydrolysis of the sulfonyl chloride groups followed by electrostatic binding of cations in the resulting polysulfonate films; and 5) Incorporation of emitting chromophores into the polymeric films.

As noted above, these polymers can be cast onto electrodes as films by simple evaporation of polymer solutions. Another method of attaching redox polymer films onto electrodes is by electropolymerization. Reductive electrochemical polymerization of vinyl containing complexes of iron, ruthenium and osmium has been well studied.[11] We recently described a general technique for oxidative electropolymerization to produce electrodes coated with electroactive polymers.[12] In this study we found that polypyridyl complexes of ruthenium which contain aromatic amine groups, e.g., $[(bpy)_2Ru(4-pyNH_2)_2]^{2+}$, (4-$pyNH_2$ = 4-aminopyridine); $[(bpy)_2Ru(3-pyNH_2)_2]^{2+}$, (3-$pyNH_2$ = 3-aminopyridine); $[(bpy)_2Ru(5-phenNH_2)]^{2+}$, (5-$phenNH_2$ = 5-amino-1,10-phenanthroline); $[(bpy)Ru(5-phenNH_2)_2]^{2+}$; and $[Ru(5-phenNH_2)_3]^{2+}$ undergo electrochemically induced, oxidative

polymerization reactions. The resulting polymers form fairly stable, electrochemically active films on the oxidizing electrode, which can be Pt, SnO_2 or vitreous carbon. Complexes containing only one amine substituent are difficult to polymerize, but can be copolymerized with $[Ru(5-phenNH_2)_3]^{2+}$. Evidence suggests that the polymerization processes is ligand based and affected by addition of base to the polymerization media. Stability studies indicate that the films lose electrochemical activity upon repeated oxidative cycling in the presence of trace H_2O.

Although preparation and characterization of redox site incorporated polymer films has been a major goal of our research, we have also attempted to compare polymer-bound redox sites to monomeric analogues in the role of an excited state chromophore and of a catalyst.

An excited state photoelectrochemical cell for the production of O_2 based on oxidative quenching of $Ru(bpy)_3^{2+*}$ by $Co(ox)_3^{3-}$ (ox^{2-} is oxalate $C_2O_4^{2-}$) in acidic solution has been reported.[13] To test a Ru-bpy containing polymer in the role of chromophore, an analagous cell was set up in which a $(bpy)_2Ru(PVP)_2^{2+}$ film was deposited onto a platinum flag and employed as a photoelectrode.[14] The quenching of the Ru-bpy chromophore on the photoelectrode by $Co(ox)_3^{3-}$ was found to be analagous to that of the homogeneous $Ru(bpy)_3^{2+}$ system. A typical photocurrent of 45 $\mu A/cm^2$ was observed with the film. Unlike the homogeneous cell, where the photocurrent was observed to fall off with time due to reduction of $Ru(bpy)_3^{3+}$ by released oxalate, the photocurrent in the heterogeneous system remained fairly stable over the period of 2-3 hours if sufficiently high concentrations of $Co(ox)_3^{3-}$ were used. At low quencher concentrations (<1.0 x

10^{-4} M), the films are less stable, apparently owing to the photochemical loss of PVP.

To study a polymeric redox system in the role of catalyst, we chose to utilize the ruthenium dimer, $(bpy)_2Ru^{III}(OH_2)ORu^{III}(OH_2)(bpy)_2^{4+}$, whose oxidized form is a known catalyst for the oxidation of H_2O to O_2,[15] to explore the oxidation of Cl^- to Cl_2.[16] In solution, starting with the one electron oxidized form of the dimer, $(bpy)_2Ru^{III}(OH_2)ORu^{IV}(OH)(bpy)_2^{4+}$, oxidation either chemically (using excess $Ce^+(IV)$) or electrochemically (using a reticulated vitreous carbon electrode potentiostated at +1.20 V vs. SCE) resulted in generation of Cl_2 gas. The electrocatalytic reaction is notable, since no significant production of O_2 was observed. The catalytic Cl^- oxidation occurs with relatively high current densities near the thermodynamic potential for the Cl^-/Cl_2 couple (+1.13 V vs. SCE, pH 0-3).

To construct a modified electrode incorporating the μ-oxo bridged Ru-Ru dimer, we used the technique of ion-exchanging the dimer into sulfonated polystyrene. To generate the polymer, p-chlorosulfonated polystyrene deposited on a glassy carbon electrode was treated first in basic aqueous solution (pH>9), then soaked in a solution of the dimer. The properties of these electrodes have been studied in aqueous solution as a function of pH, electrolyte, and polymer morphology.[17] In acid solution, slow charge transport in the film partially quenches the oxidation of the complex beyond the [Ru(III),Ru(III)]state. This quenches the oxidation of water to oxygen normally observed for the complex in acid solution but not the oxidation of chloride to chlorine. The reductive cleavage of the complex is observed leading to a film containing the corresponding monomer, cis-$(bpy)_2Ru(H_2O)_2^{2+}$. The monomer displays considerably

different charge transport properties than the dimer in the polymer matrix. The electrocatalytic oxidation of chloride to chlorine by these modified electrodes was investigated. Rotated disc experiments show limiting currents dependent on chloride concentration but independent of rotation rate. The electrocatalytic oxidation is characterized by fast rates and poor catalyst stability.

In summary, our work has progressed along two themes, mixed-valence chemistry and redox-site containing polymers. In mixed-valence dimers, we have probed the energy of the IT band in terms of inner-sphere reorganization energy, the internal energy difference between redox sites, and contributions from spin-orbit components. We have also observed metal to metal charge transfer in optically prepared mixed-valence dimers. In metallopolymers, we have studied the preparation and characterization of several types of polymers, as well as their usefulness in photoelectrochemical and catalytic applications.

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